Metallurgical Reaction Philosophies of Transferred-arc Plasma Furnaces

by

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Synopsis

Proposed metallurgical models of two basic types of transferred-arc plasma furnaces that are potentially suitable for use as metallurgical reactors in the production of ferrochromium are evaluated. For furnaces with the molten-bath anode, the large dissipation of energy on the surface of the bath requires a sequence involving a 'bath' reduction reaction. For furnaces with the ancillary anode, the ability of the furnace to deliver reactants direct into the plasma zone at a controlled rate requires an 'in-flight' reduction reaction.

INTRODUCTION

One of the recent advances in mineral science and technology that has received considerable attention in the literature is the rise of a new generation of pyrometallurgical furnace systems, namely plasma furnaces[1-6]. The expected development of these furnaces for commercial metallurgical applications was disappointingly slow at first, but transferred-arc plasma furnaces very recently made great strides towards commercial reality in pyrometallurgical applications for remelting and smelting. More particularly, it was the suitability of these plasma furnaces as melting furnaces that brought about this development, and large-scale transferred-arc plasma furnaces are in operation as commercially feasible remelting furnaces. Their application as smelting furnaces has been hampered by a lack of fundamental understanding of the extent to which the thermodynamic and kinetic aspects of the process chemistry can be influenced by the plasma, and of how this information can be used in the optimization of the overall process. By 1980, because the parameters influencing the effective use of plasma-arc energy in this metallurgical environment had remained undefined, the Council for Mineral Technology (Mintek) initiated a fundamental investigation of the conversion of electrical energy to metallurgically usable thermal energy in transferred-arc plasma furnaces. Mintek also sponsored studies by Maske[7] at the Plasma Technology Group, Mineral Resources Research Center, University of Minnesota, which included the identification of metallurgical models of the specific transferred-arc plasma furnaces used.

Essentially, there are two basic types of transferred-arc plasma furnaces: those with an ancillary anode, and those with a molten-bath anode[6]. As metallurgical reactors, both types of furnace are potentially superior to conventional furnaces[8,9] in that the effective transfer of energy to different stages of a reduction–reaction sequence can be accomplished in a large number of ways. Even though the underlying principles of arc physics and chromium chemistry apply to both reactor configurations, the parameters influencing the effective use of plasma-arc energy lead to two distinct metallurgical models.

MOLTEN-BATH ANODE

In the configuration with a molten-bath anode, the electrical connection of the anode is embedded in the furnace hearth refractories. The arc is thus induced to become attached to the surface of the bath, and the resulting conditions are very favourable for the transfer of energy to the slag–metal bath without damage to the side-wall refractories. The use of such an open bath of liquid slag and metal permits far greater freedom and control over the process metallurgy than is possible in the choke-fed submerged-arc furnace. As a consequence, extremely encouraging metallurgical results are possible.

In this fundamental investigation it was found that, by the imposition of the correct balance of

furnace parameters (related to both reduction reactions and to the plasma arc), slags in which the Cr_2O_3 content was less than 3 per cent and the FeO content less than 1 per cent could be produced consistently and predictably (Table 1). This is in contrast to the results obtained in conventional submerged-arc practice, where typical slags assay as Cr_2O_3 in the region of 14 per cent and FeO, 7 per cent. The composition of the alloy could also be altered by the encouragement of appreciable amounts of $(CrFe)_{23}C_6$ to form together with the more common $(CrFe)_7C_3$ phase. This atypical lower-carbide ferrochromium can accommodate some silicon[10]. Besides ferrochromium alloys with more typical compositions, alloys with a silicon content of up to 11 per cent and a carbon content of only 4 per cent can therefore be produced.

TABLE 1

Chemical analyses of the slags and metals produced in smelting campaign UM/2

(All the analyses are expressed in percentages by mass)

Pour no.	Slag			Metal				
	Mass kg	Cr_2O_3 %	FeO %	Mass %	Cr %	Fe %	Si %	C %
1	1,2	2,56	1,72	10,5	47,7	39,5	7,35	3,8
2	4,3	1,43	0,80	0,1	47,4	37,4	8,02	3,6
3	5,6	2,35	0,68	0,0				
4	3,3	2,12	0,83	7,7	50,4	39,0	5,55	4,3
5	4,8	2,60	0,68	0,3	51,0	36,4	7,04	4,6
6	5,0	1,47	1,13	0,1	47,5	31,9	11,1	4,2
7	4,7	2,00	0,60	0,0				
8	5,4	3,62	1,07	1,9	51,4	37,0	6,03	5,0
9	5,7	4,92	1,46	4,3	52,0	37,4	4,94	4,7
10	4,9	3,58	1,03	6,3	53,6	35,6	4,33	5,0
11	4,3	4,67	0,93	10,8	52,9	38,9	2,83	5,0
12	6,9	14,7	2,61	3,8	50,4	42,1	0,91	5,1
13	4,6	8,33	1,22	2,8	52,1	35,7	1,75	6,5
14	4,4	17,8	3,88	3,0	49,5	44,1	0,48	6,2
15	5,4	17,5	1,11	2,7	50,8	39,9	0,68	6,2
16	3,3	3,93	1,21	0,0				
17	4,6	2,30	0,50	0,0				
Dig-out top	4,3*	27,8	6,22	53,5*				
Dig-out bottom		9,94	6,07		52,5	37,2	4,17	5,6

* Total mass

The chromite-smelting trials that were undertaken at Mintek in a specially designed 100 kW water-cooled, transferred-arc plasma furnace with a molten-bath anode provided the basis for the metallurgical smelting model of a molten-bath anode. This model is illustrated schematically in Figure 1, and is briefly evaluated in terms of the parameters that were found to affect the optimum smelting conditions for chromite.

Arc-attachment zone

The anodic-arc attachment on the open bath of liquid slag and metal is not static, but wanders
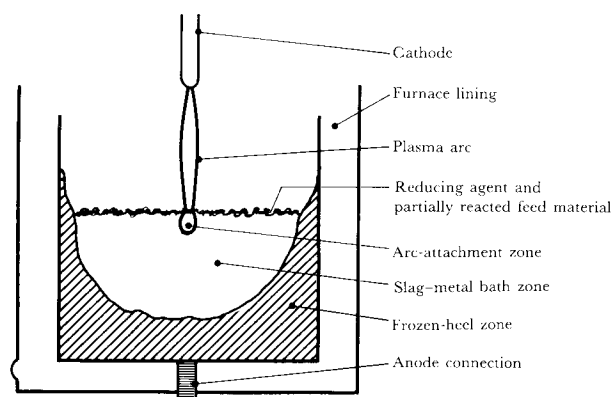
Figure 1. Schematic diagram of the zones thought to exist in a transferred-arc plasma furnace with a molten-bath anode used for the production of ferrochromium

rapidly over a comparatively small area of the bath surface (unless moved externally). It appears that the movement of the arc attachment is not purely random, and the arc tends to favour an attachment to particles of reducing agent floating on the open bath. Owing to its naturally induced rapid motion, the attachment itself and its zone of influence cause severe energy fluxes through a relatively small area of the bath surface.

Although the dissipation of intense energy at the localized arc attachment provides the energy necessary to sustain the *status quo* of the molten bath, the energy flux over this small area is too great to drive the metallurgical reactions efficiently in the arc-attachment zone. A deterimental metallurgical consequence of these severe energy fluxes is that they cause some reducing agent to be lost from the system. This condition is compounded when scale-up is considered, since the magnitude of the energy dissipated at the local attachment increases disproportionately to the area of the attachment. Any imposed furnace parameter that increases the magnitude of the energy dissipated at the anode or that favours arc attachment to the particles of reducing agent has been found to have an adverse effect on the metallurgical performance of the reactor. When increased arc powers (Table 2) or larger particles of reducing agent (Table 3) were employed (all other furnace parameters being controlled within their limits of influence), dark-blue, glassy slags rich in Cr_2O_3, although low in FeO, were obtained. The carbon efficiency detailed in Tables 2 and 3 is the ratio (expressed as a percentage) of the amount of carbon required for all the reduction reactions (Cr,Fe,SI) and for the provision of the carbon dissolved in the ferrochromium to the amount of input carbon, and can be seen to decrease with an increasing loss of reducing agent from the system. A mineralogical investigation of these slags indicated clearly that there had been a complete dissolution of the chromite[11]. The chromium recoveries were poor because the reducing agent available (after dissolution) was insufficient to ensure that

the partial pressures of oxygen would be low enough for the complete reduction of the CrO.

TABLE 2

The effect of arc power on the Cr_2O_3 and FeO in the slag and on the excess carbon, when nitrogen is used as the primary plasma gas with coarse chromite particles and a siliceous recipe fed at 9,3 ($\pm$ 0,5) kg/h

Heat no.	Average arc power kW	Cr_2O_3 % (by mass)	FeO % (by mass)	Transformer tap position no.	Carbon efficiency* %
UM 2/6	50,3	1,47	1,13	9	110
UM 2/7	51,9	2,00	0,60	9	110
Average	51,1	1,74	0,87	9	110
UM 2/8	58,8	3,62	1,07	10	97
UM 2/9	58,1	4,92	1,46	10	92
Average	58,5	4,27	1,27	10	95
UM 2/12	61,2	14,7	2,61	11	74
UM 2/13	61,3	8,33	1,22	11	86
Average	61,3	11,52	1,92	11	80

* The ratio of the amount of carbon required for all the reduction reactions and for the provision of the carbon dissolved in the ferrochromium to the amount of input carbon

TABLE 3

Effect of particle size of reducing agent at an average arc power of 59 ($\pm$1)kW on the Cr_2O_3 and FeO in the slag when nitrogen is used as the primary plasma gas with coarse chromite particles and a siliceous recipe

Heat no.	Size range of reducing agent mm	Cr_2O_3 % (by mass)	FeO % (by mass)	Carbon efficiency %
UM 2/8	<3 >0,25	3,62	1,07	97
UM 2/9	<3 >0,25	4,92	1,46	92
Average	<3 >0,25	4,27	1,27	95
UM 2/14	<4,5 >0,7	17,8	3,88	71
UM 2/15	<4,5 >0,7	17,5	1,11	75
Average	<4,5 >0,7	17,65	2,50	73

However, the rate at which the carbon is lost can be effectively lowered by a reduction of the particle size of the reducing agent, injection of powdered reducing agent into the bath, feeding of the reducing agent to the periphery of the molten bath, or external movement of the anode-arc attachment. Furthermore, modifications that disperse the anodic arc energy (such as the use of argon instead of nitrogen or a cathode of different design) also tend to reduce the rate at which carbon is lost at the higher arc powers. These carbon losses must be retarded to the extent that, after

dissolution of the chromite has taken place in the slag bath, sufficient reducing agent remains available to ensure that the partial pressures of oxygen are low enough for subsequent reduction of the CrO.

Slag–metal bath zone

The reduction reactions were carried out in an open bath of liquid slag and metal since no attempt was made to entrain the reactants in the arc. The average temperature of the bulk of this furnace zone, and therefore of the reaction temperature, was dictated by the composition of the slag in the water-cooled furnace. The intense energy dissipated at the arc-attachment zone provides the energy necessary to sustain a bath of molten slag, even if extremely high liquidus temperatures are dictated by the composition of the slag. Slags with approximate liquidus temperatures of over 2000 °C were tapped. However, the size of this bath, and therefore of the smelting zone, varies, depending on the energy requirements of the process, the heat losses from the open bath, and the heat-capacity requirements of the bath. The influence of flux additions on the ferrochromium produced is illustrated in Table 4 (all other furnace parameters being controlled within their limits of influence). Basic recipes that increased the liquidus temperature of the slag resulted in high silicon levels in the ferrochromium product, which indicates that the reduction reactions were carried out at significantly higher temperatures. Acidic recipes that decreased the liquidus temperature of the slag resulted in lower reaction temperatures and the production of a more typical ferrochromium. It was found that the slag could not be significantly superheated in the water-cooled furnace simply by an increase in arc power. However, the size of the bath increased, as did the rate at which carbon was lost from the arc-attachment zone (Table 2). The rate of chromite dissolution occurring in this zone must be balanced with the rate at which carbon is lost from the arc-attachment zone if high recoveries of chromium are to be obtained.

TABLE 4

Effect of flux additions on the ferrochromium product (as percentage by mass)

Flux additions	Heat numbers	Average slag basicity*	Average metal analyses			
			Cr %	Fe %	Si %	C %
Basic	UM2/2,3	1,4	47,4	37,4	8,0	3,6
Acidic	UM2/8,9	0,9	51,7	37,2	5,4	4,9

* The basicity is defined as the ratio of MgO plus CaO to the SiO_2 in the slag

Frozen-heel zone

A natural region of frozen slag and metal that separated the open bath from the containing furnace

TABLE 5

Average energy balance during feeding in the smelting campaign UM2

Heat no.	Arc voltage V	Arc current A	Arc power kW	Calorimetrically measured power					Temperature of side walls °C	Average feed rate kg/h
				Total kW	Anode %	Hearth %	Side walls %	Roof %		
1	76,2	790	60,3	38,2	11,8	61,8	18,6	8,0	717	9,1
2	80,1	758	60,7	40,0	13,2	63,4	16,5	6,8	668	9,3
3	77,9	776	60,5	40,0	10,3	65,7	17,1	7,0	716	9,2
4	77,9	770	59,7	39,2	10,8	63,0	18,4	7,8	777	9,3
5	77,9	770	60,0	39,8	12,5	63,4	16,7	7,4	706	9,4
6	76,0	663	50,3	36,6	12,3	64,4	16,3	7,0	625	9,8
7	73,5	708	51,9	34,8	13,0	65,1	15,6	6,4	577	9,8
8	82,4	698	58,8	38,3	12,5	63,6	16,9	7,0	689	8,8
9	82,7	714	58,1	38,0	5,0	64,8	21,7	8,5	778	9,3
10	78,9	768	60,5	36,1	5,5	65,0	21,5	7,9	670	13,0
11	76,6	799	59,6	37,8	6,2	67,1	19,4	7,2	657	14,1
12	92,2	667	61,2	44,3	10,4	66,6	16,3	6,7	639	9,1
13	91,4	685	61,3	44,4	12,8	64,2	16,3	6,7	630	9,1
14	75,9	799	60,6	42,0	14,6	60,7	16,8	7,9	637	8,4
15	75,9	785	60,1	40,2	14,3	61,0	16,9	7,8	620	8,3
16	79,8	729	57,9	42,4	15,0	63,7	14,9	6,3	593	7,6
17	77,6	773	59,9	40,8	12,9	65,4	15,3	6,5	579	7,5

shell was formed and was identified as the third integral furnace zone of the configuration with a molten-bath anode. This zone is the interface between the bath and the surrounding refractories, and provides the necessary protection for the anodes embedded in the hearth refractories and for the refractories themselves. As the intense energy dissipated at the anodic-arc attachment would melt an unprotected anode in a matter of minutes, a necessary operating philosophy for the specific configuration investigated is the control of the frozen heel in order to protect the integrity of the anodes. The fact that the attack on the side-wall refractories was minimal, even though slags of very different basicities and liquidus temperatures were tapped, is also largely ascribed to the protection afforded by this zone.

The results of the energy balance recorded during the campaign previously discussed are detailed in Table 5. The significant change in the distribution of the calorimetrically measured energy that occurred as a result of the interruption during the eighth pour indicates that any deviation from a steady smelting routine results in changes in the *status quo* of this zone and distorts the proportion of arc energy reporting to different furnace regions. These distortions are not immediately self-rectifying if smelting is continued, and, as they cause the performance of the furnace to change, the production of a consistent metal product at a uniform energy consumption requires a return to the original *status quo* in this zone before the smelting operation is continued.

ANCILLARY ANODE

In the transferred-arc plasma furnace with a molten-bath anode, the feed materials could not be entrained into the plasma arc, and therefore

could not be exploited for the reduction of the chromite within the plasma zone, namely 'in flight'. However, when the anodic-arc attachment was removed from the molten bath, the transferred-arc plasma furnace with an ancillary anode and a controlled rotation of the arc allowed the reactants to be delivered direct into the plasma-arc zone. As a result, the chromite could be reduced within the plasma-arc zone of these furnaces. A sample of the results obtained in this fundamental investigation is given in Table 6. Owing to the difficulty involved in the separation of the incompletely smelted product, the analyses of the metals did not add up to 100 per cent and were reproportioned, recognized assumptions being taken into account. The imposition of the correct balance of furnace parameters (related to both reduction reactions and to the plasma arc) made it possible for

TABLE 6

Products of the most successful heats of each chromite-reduction campaign in the ancillary-anode furnace

Campaign no.	Non-metallic product % (by mass)		Metallic product % (by mass)				Recoveries to the metal, %	
	Cr_2O_3	FeO	Cr	Fe	Si	C	Cr	Fe
1	22,6	12,4	48,7	42,1	1,7	7,4	42,5	50,7
2	23,4	12,6	46,8	42,5	3,5	7,2	32,7	41,9
3	15,2	7,03	35,8	51,6	6,8	5,6	24,0	46,5
4	11,3	5,2	47,3	39,1	9,8	3,8	50,0	61,3
5	12,4	5,8	45,4	41,6	8,6	4,5	29,3	41,8
6	25,7	13,1	42,7	41,1	11,8	4,4	28,3	39,6
7	17,4	8,3	45,6	37,0	12,8	4,6	51,9	61,8
8	11,4	4,6	46,7	37,2	9,9	6,1	48,9	62,4

50 and 60 per cent respectively of the total chromium and iron oxide within this plasma-arc zone to be reduced. This ability, namely for the reduction to be carried out within the arc-column region of the plasma, dramatically influenced the parameters that control the effective use of plasma-arc energy.

The reduction of chromite was undertaken in two different 100 kW sustained-shockwave plasma reactors at the Minerals Resources Center of the University of Minnesota, and provided the basis for the metallurgical model of the ancillary anode. This model is illustrated schematically in Figure 2, and is evaluated briefly in terms of the parameters found to affect the optimum reduction of chromite within the plasma arc itself.
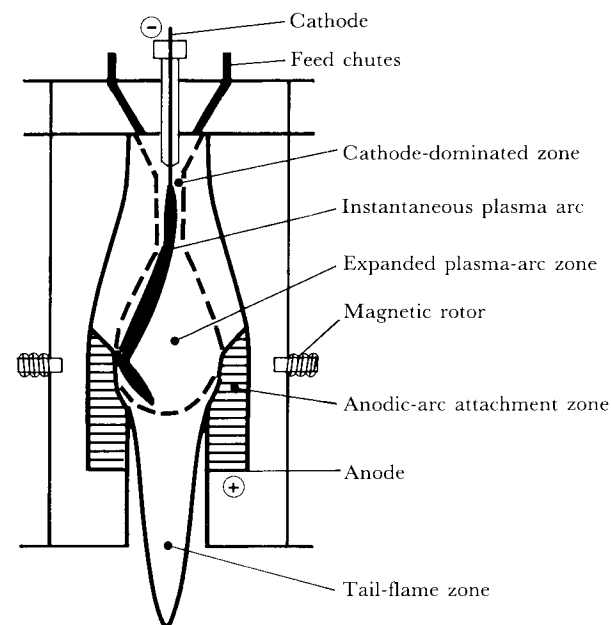

Figure 2. Schematic representation of the zones thought to exist in a transferred-arc plasma furnace with an ancillary anode

Cathode-dominated zone

The naturally constricted arc root at the cathode induces a gas-pumping action (cathode jet), which gives the arc the ability to assume a seemingly stationary vertical position pointing away from the cathode, regardless of conditions elsewhere in the furnace. This naturally induced flow causes the gases surrounding the cathode to be drained into the arc, and allows the reactants to be entrained in the plasma. Moreover, the entrainment is very sensitive to the geometrical arrangement of the feed chutes in relation to the cathode tip. If the proper geometrical arrangement is not established, the reactants will bypass the expanded plasma-arc zone and undergo only minimal treatment during their passage through the entire reactor[12]. At a certain distance away from the cathode, the motion of the arc is no longer determined solely by the cathode jet, and several factors (including the cathode jet) are responsible for the motion of the arc as it 'skews' off and wanders rapidly over the surface of the anode. Although entrainment must be effected at the cathode-dominated zone for the reactants to be treated efficiently, the motion of the arc, which is dominated by the cathode jet, allows only a very small percentage of the reactants to interact with the plasma arc and to be treated in this zone.

Expanded plasma-arc zone

Except within the cathode-dominated zone, the instantaneous arc does not assume any fixed position, but wanders rapidly within the expanded plasma-arc zone, causing the entire zone to undergo a certain amount of ionization.

These seemingly random positions assumed by the arc are biased by several controllable furnace parameters (e.g., arc rotation, cathode design, and feed rate) that allow the boundary of the expanded plasma-arc zone to be defined and controlled. However, the various positions assumed by the arc within this zone are not controllable, and the exact location of the instantaneous arc within this zone changes continually. These conditions allow the reactants to interact efficiently with the plasma arc.

Techniques that increased the relative volume of this zone (e.g., an increased feed rate, increased rotation, decreased flow of primary plasma gas) or that favoured reaction within this zone (e.g., the addition of oxygen with the carrier gas) were found to have a controlling influence on the chromite recoveries achieved. In one test, a decrease of 40 per cent in the flowrate of the primary plasma gas resulted in an increase in the recoveries of chromium and iron by 89 and 94 per cent respectively; the chemical composition of the metallic and non-metallic furnace products remained largely unaffected (Table 7).

TABLE 7

Effect of flowrate of primary plasma gas on products of in-flight reduction

Flowrate of primary plasma gas l/min	Non-metallic product % (by mass)						Metallic product % (by mass)					Recovery %	
	Cr_2O_3	FeO	SiO_2	CaO	MgO	Al_2O_3	C	Cr	Fe	Si	C	Cr	Fe
48	25,9	13,9	27,0	1,11	10,5	13,0	10,1	40,3	35,8	13,9	3,8	15,0	20,4
27	25,7	13,1	28,7	1,68	12,0	14,6	7,0	39,2	37,7	10,8	4,0	28,3	39,6

However, several difficulties associated with an increase in the relative volume of this zone adversely affect the conversion of electrical energy to metallurgically usable energy. When this zone was increased at the relative expense of the cathode-dominated zone, very severe refractory damage occurred, since the instantaneous arc can attach itself to the refractory above the graphite anode. Although this condition largely cripples the tail flame, no metallurgical problems were encountered.

Anodic-arc attachment zone

The actual arc attachment to the anode is dynamic and not only rotates rapidly round the internal surface of the annular anode, but also moves continually up and down over the surface. Besides the important influence on the expanded plasma-arc zone of arc rotation or, more precisely, of the induced magnetic force rotating the most probable region of arc attachment to the anode, rotation provides the necessary protection to the anode. Quite clearly, the use of a slag-forming recipe resulted in some reduction of chromite on the surface of the anode in a manner similar to that in a 'falling-film' plasma reactor, but the anodic-arc attachment zone does not exert the same controlling influence on the chromite recoveries as the expanded plasma-arc zone does. When the anode design was changed from a segmental water-cooled configuration to an annular configuration with a much larger surface area, the recoveries of chromium and iron remained largely unchanged. However, the chemical composition of the ferro-chromium product appeared to be sensitive to the particular configuration. With the water-cooled configuration, the alloy averaged a silicon content of 3,2 per cent by mass, whereas, with the annular anode, the average silicon levels were over 10,6 per cent by mass, which implies that the reduction temperatures were higher.

Tail-flame zone

Although the tail flame can be exploited by the use of the enthalpy of the arc-heated gas to sustain a molten pool in a crucible immediately below the anode, this was not attempted, since this investigation was focused on the effect of the entrainment of the feed materials into the plasma arc on the reduction of chromite.

CONCLUSIONS

The experimental investigations were undertaken in an attempt to evaluate the mechanisms controlling the effective usage of plasma-arc energy within the constraints of the process chemistry of ferro-chromium production. This approach led to the identification of metallurgical models that apply to the experimental transferred-arc plasma furnaces investigated on a 100 kW scale. Although restricted to this application, these models provide a

necessary insight that can be of assistance in the design of transferred-arc plasma furnaces for the production of ferrochromium, as well as in the identification of the metallurgical approach needed for the realization of the optimum smelting conditions in these plasma-arc reactors.

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